

Nucleation of Tropospheric Aerosols: A Joint Laboratory and Theoretical Study of Multicomponent Systems

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Motivation

- Tropospheric aerosols play important roles in:
human health, radiation balance, pollutant scavenging, visibility, oxidant concentrations
- Understanding of fundamental aerosols processes is lacking:
e.g., aerosols are major source of uncertainty in models of radiative forcing, role of heterogeneous reactions unclear, mechanisms of nucleation unclear
- Nucleation important because it creates new particles, increasing aerosol number:
most important when aerosol particle number is low and precursor concentrations are high
- Nucleation may also be important because it creates ultrafine particles (< 50 nm):
ultrafine particles under scrutiny by EPA because of health risks
- Current theories for nucleation (e.g., classical nucleation theory) have shortcomings:
predict threshold for nucleation but not magnitude, nucleation in multicomponent systems poorly described, etc.

Nucleation of Tropospheric Aerosols:

A Joint Laboratory and Theoretical Study of Multicomponent Systems

Molecular-Scale Simulations

- develop models of molecular interactions controlling cluster formation
- develop methods for calculating the rate constants for cluster formation and decomposition (condensation & evaporation)
- model kinetics of nucleation as function of temperature and component concentration

*model validation
and refinement*



interpretation



Laboratory Experiments

- use laminar flow tube reactor to measure nucleation rates as a function of temperature and component concentration
- use ion cyclotron resonance and mass spectrometric techniques to measure composition of nucleated particles

*understand details
of nucleation
mechanisms*



*improve phenom-
enological models*



*reduce uncertainties
in atmospheric
models of aerosols*



*select systems for
lab studies*



*validate nucleation
mechanisms in
troposphere*



Atmospheric Chemistry Modeling and Field Studies

develop an understanding of aerosol dynamics, including the role of nucleation on aerosol formation and composition

Nucleation of Tropospheric Aerosols:

Molecular simulations of cluster formation in multicomponent systems

BC Garrett, SM Kathmann, LX Dang, KA Peterson, GK Schenter, SS Xantheas

Molecular Interactions

- Intermolecular interactions characterized by high-level ab initio electronic structure calculations
- Interaction energies fitted to many-body analytic functions

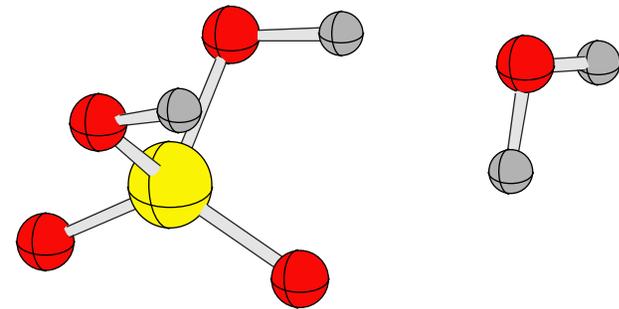
Cluster Formation and Decomposition Rates

- New molecular theory has been developed - rate constants for cluster evaporation obtained directly using variational transition state theory and statistical mechanical simulations
- Condensation rate constants obtained by detailed balance from evaporation rate constants and equilibrium cluster distributions
- Cluster distributions obtained by statistical mechanical simulations

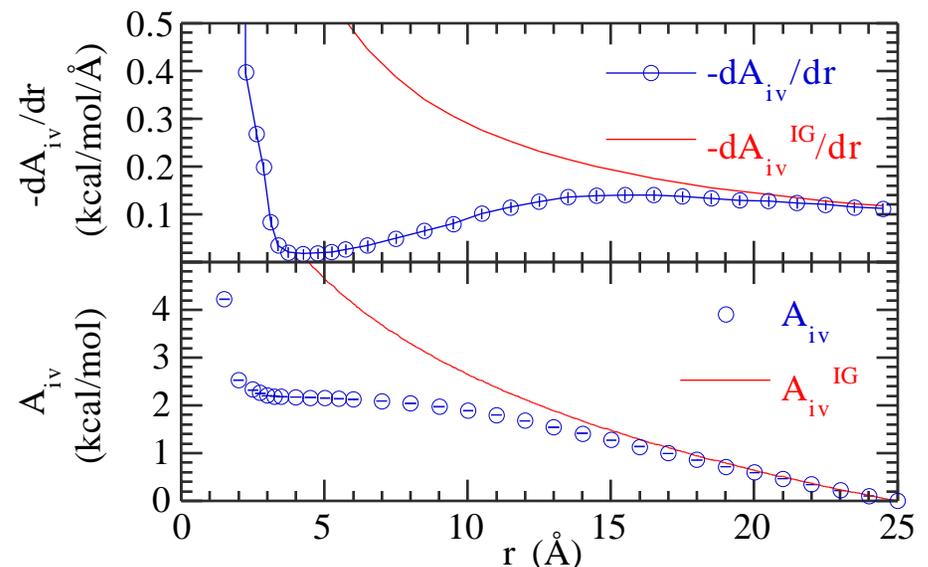
Nucleation Kinetics

- Ordinary differential equations for cluster concentrations solved numerically

Sulfuric acid - water interaction (binding energy 13.1 kcal/mol)



Helmholtz free energy for forming $(\text{H}_2\text{O})_3$ (evaporation rate $-\text{d}A_{\text{iv}}/\text{d}r$ at minimum)



Nucleation of Tropospheric Aerosols: Experimental Studies of Multicomponent Systems

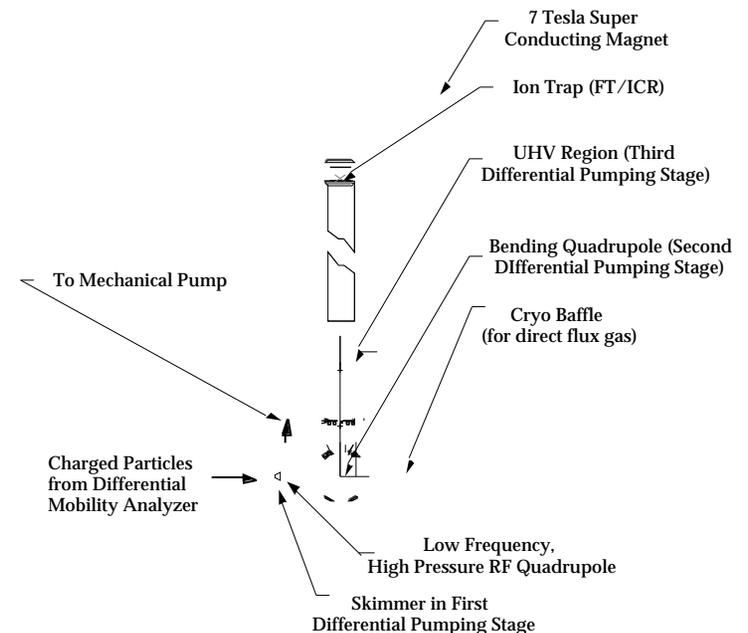
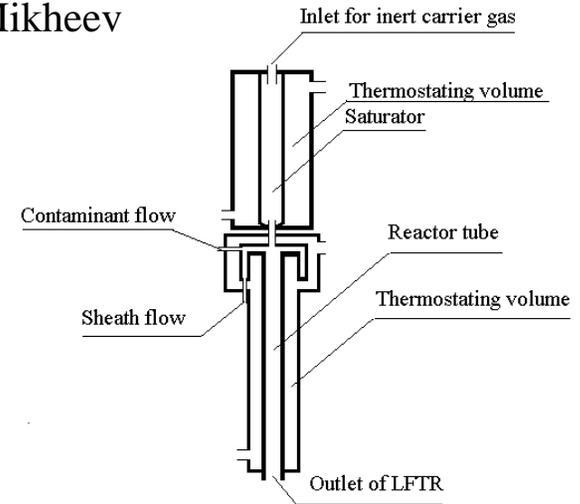
NS Laulainen, SE Barlow, and VB Mikheev

Laminar Flow Tube Reactor

- Application of the Laminar Flow Tube Reactor technique to quantify aerosol nucleation rates under controlled conditions of temperature, supersaturation, and contaminant concentrations
- Contaminant species introduced coaxially into host flow near location of maximum supersaturation
- Contaminant species may be exposed to UV or other ionizing radiation
- Each contaminant molecule can serve as a nucleation center
- Characteristics of LFTR determined through detailed computer calculations

Ion Cyclotron Resonance/Mass Spectrometer

- Nucleated particles sampled and detected by sensitive particle counter and mass spectroscopy; differential mobility analyzer provides size discrimination



Laminar Flow Tube Reactor and Ion Cyclotron Resonance / Mass Spectrometer Studies of Nucleation

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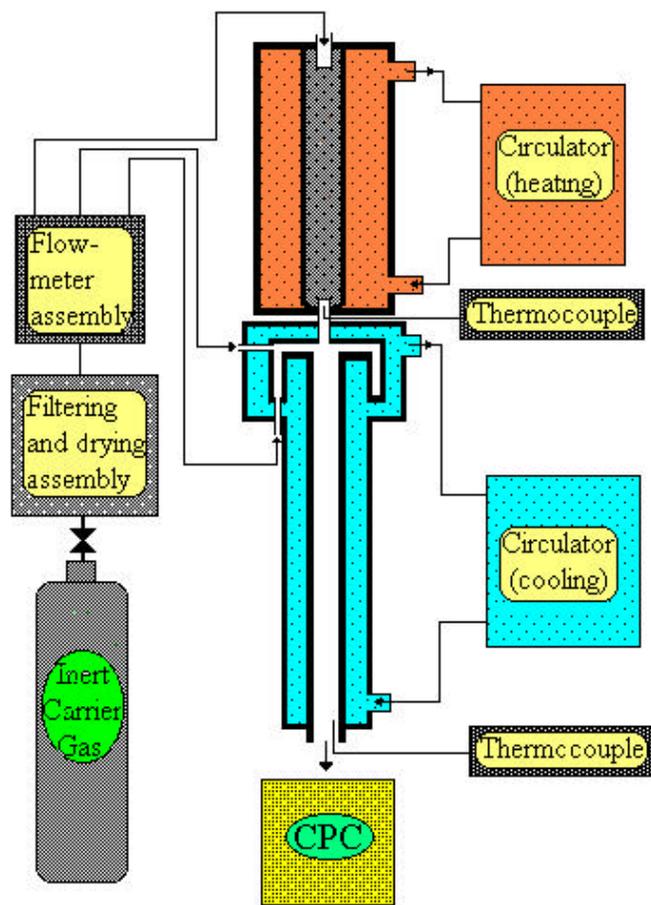
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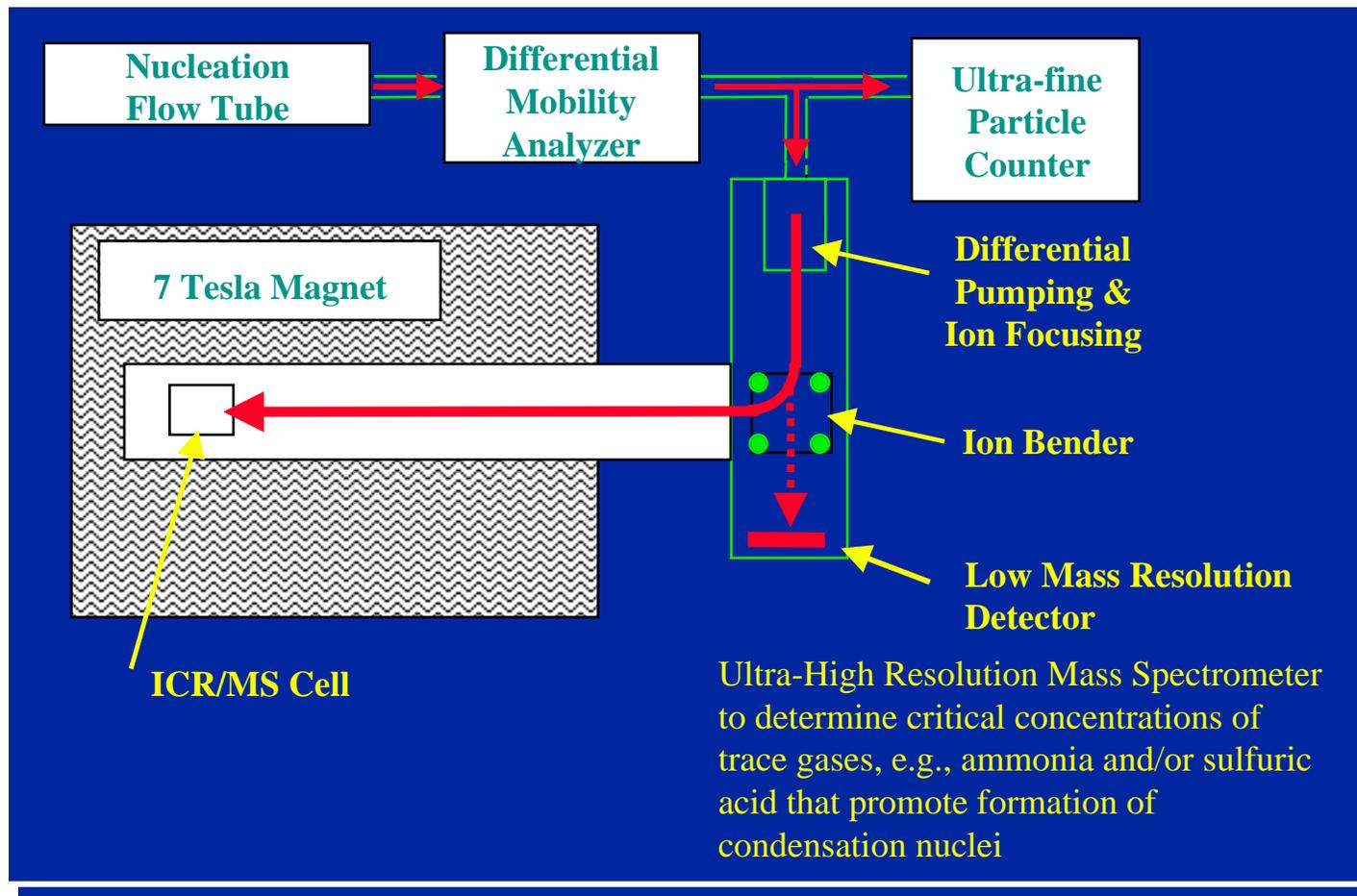
Objectives

- Measure the absolute nucleation rate of several chemical systems of interest to the formation of tropospheric aerosols, including pure water, water-sulfuric acid, water-ammonia, water-ammonia-sulfuric acid, water-various organic compounds, using a laminar flow tube reactor (LFTR) technique
- Continue to improve experimental setup (LFTR plus heater/chiller and gas-flow systems) to minimize effects of unknown/undesirable contaminants and uncertainties of thermodynamic quantities inside the LFTR on measured nucleation rates
- Verify composition of nucleated particles through improved detection techniques, including the use of a differential mobility analyzer (DMA) for particle size selection and an ion cyclotron resonance mass spectrometer (ICR/MS)

Laminar Flow Tube Reactor Schematic



Interface of Laminar Flow Tube Reactor with Ion Cyclotron Resonance/Mass Spectrometer



Combination of LFTR and ICR/MS

- Particles are produced under controlled conditions in LFTR and detected with fast response in ICR/MS
- Conduct experiment in real time to determine nucleation rate dependence upon temperature, contaminant concentration, with simultaneous MS-analysis of the particles formed in LFTR.

Difficulties

- To obtain absolute values of water nucleation rates, the carrier gas needs to be helium (Figures 1 and 2). Commercially-available CPCs (like TSI-3025A) cannot work with pure helium, so some means to provide a mixture of helium and argon with a ratio He/Ar=1/3 is needed. A modification of the LFTR near the outlet of the reactor is required to introduce a contaminant-free Ar flow.
- Nucleation in the water-He system starts very rapidly near the beginning of the condenser section of LFTR. Very accurate and precise temperature conditions need to be maintained, particularly at the union of the saturator and condenser of LFTR. Even for standard systems in the LFTR, such as dibutyl phthalate - Ar, where nucleation begins at some distance from the beginning of saturator (Figures 3 and 4), careful attention to accurate operating conditions must be made, because data obtained by different groups have shown considerable discrepancies.
- Measurement of water particle concentration itself is also a difficult task. Commercially-available CPCs can not measure pure water particles, because 1) butanol does not readily condense on them and 2) the particles may simply evaporate before they reach the counting volume. Also, there is some evidence that after water particles reach a concentration of about 10^3 to 10^4 particles/cm³, vapor exchange processes between them becomes a critical factor. Vapor from small particles migrates to the larger particles and that may change significantly the concentration value. To avoid this problem, water particles are fixed inside the LFTR immediately after they are created. This is accomplished by injecting ethylene glycol vapor into the condenser after water nucleation has occurred. (This is the same principle of the CPC, only now it occurs inside the LFTR; our recent measurements have shown that it works.)
- A new improved, version of the LFTR (Figures 5 and 6) was designed and built, which allows resolution of the problems noted above. A new measurement series is underway with the new LFTR and preliminary results are becoming available

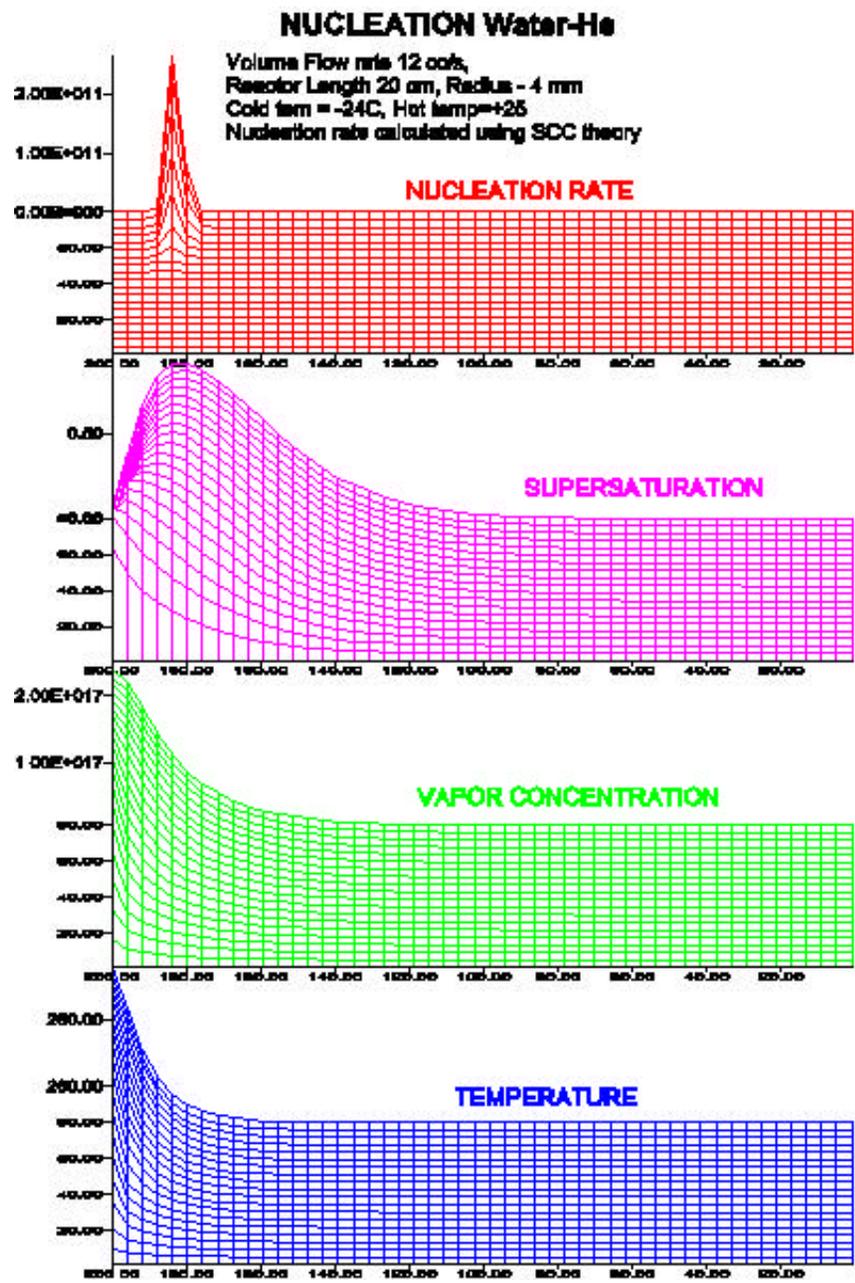


Figure 1

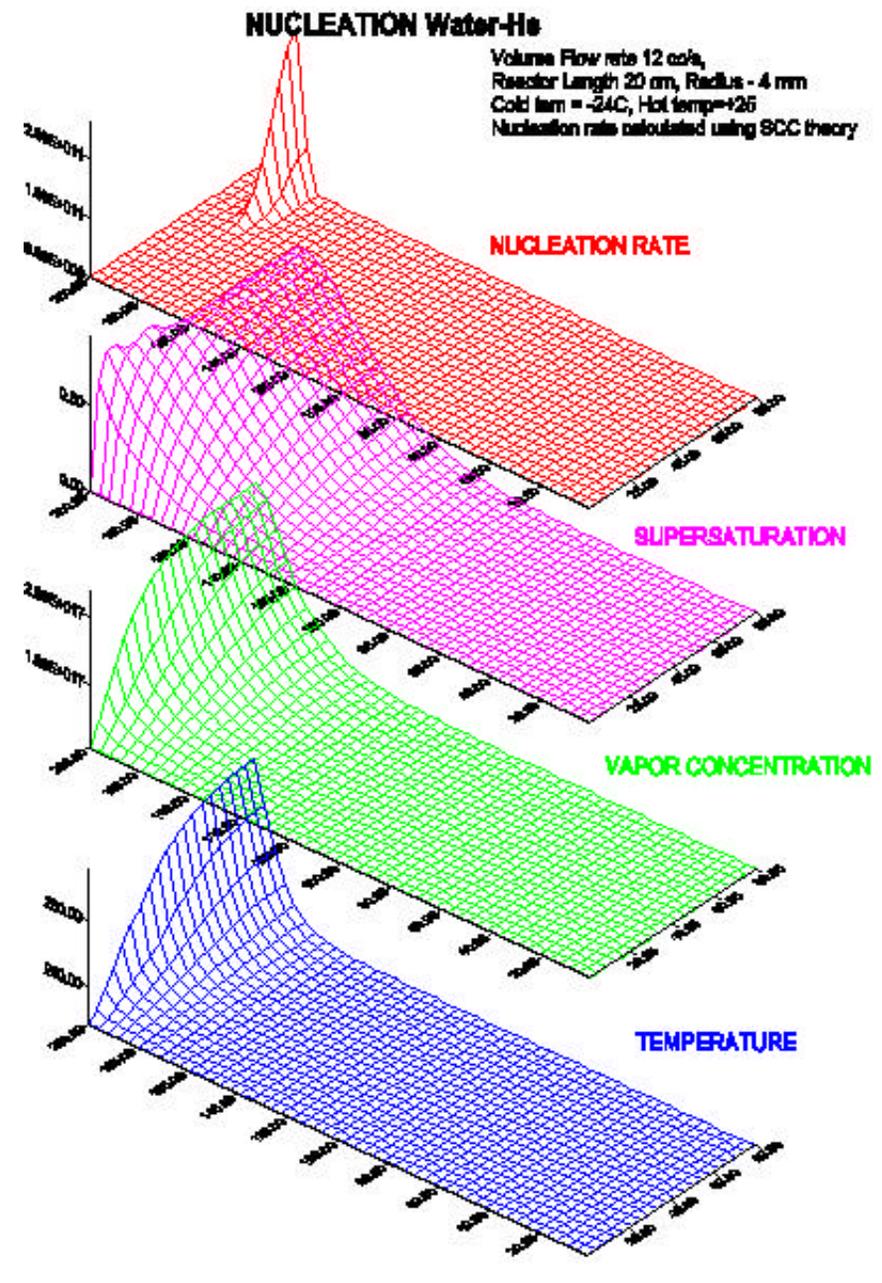


Figure 2

NUCLEATION OF DBP-Ar

Model calculations

Reactor length - 20cm, diameter 6 mm

Volume flow rates: 1 cc/s - central flow, 3 cc/s - sheath flow.

Temperature of the reactor walls +15 C

Temperature of the saturator +78 C

NUCLEATION RATE
TEMPERATURE
SUPERSATURATION
CONCENTRATION

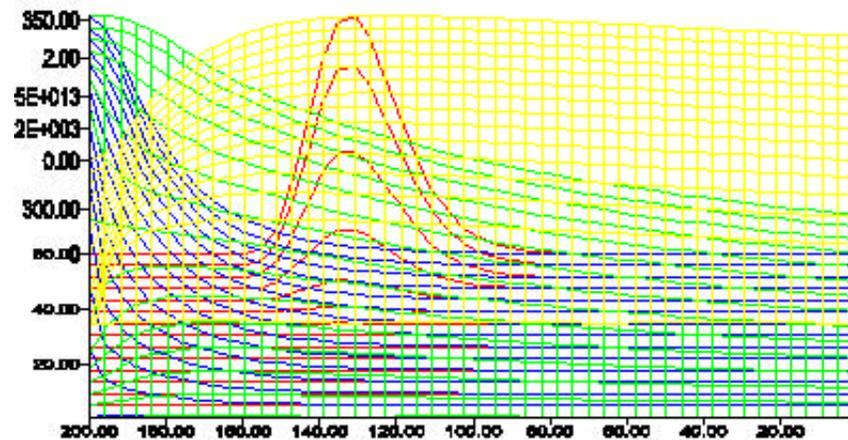


Figure 3

NUCLEATION OF DBP

Carrier-gas Argon

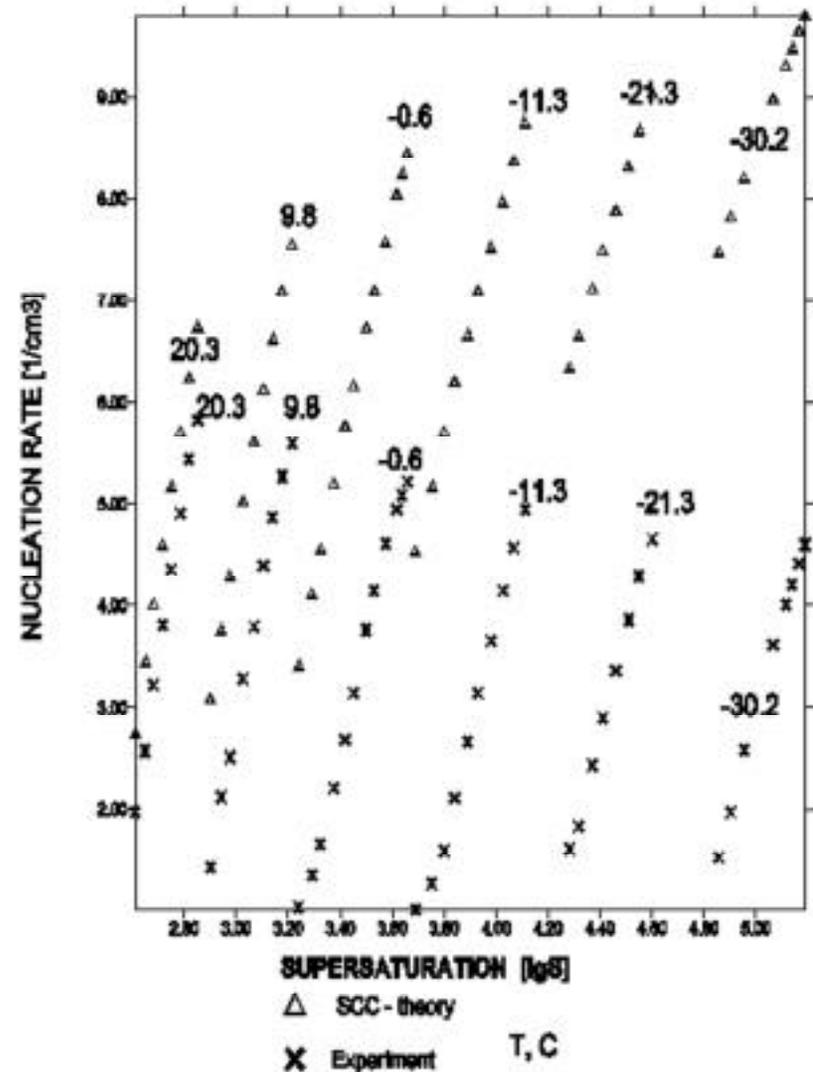


Figure 4

New Version of the Laminar Flow Tube Reactor

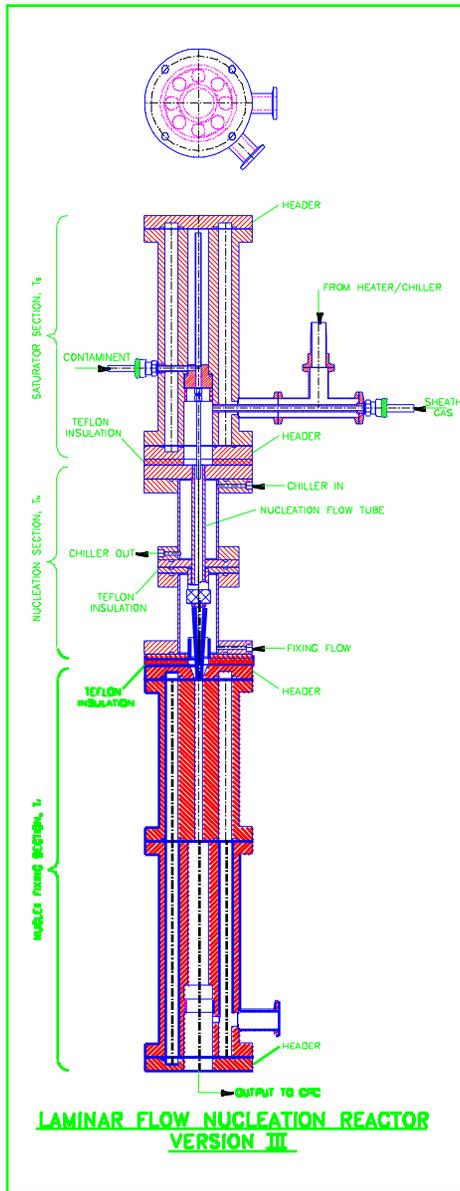


Figure 5

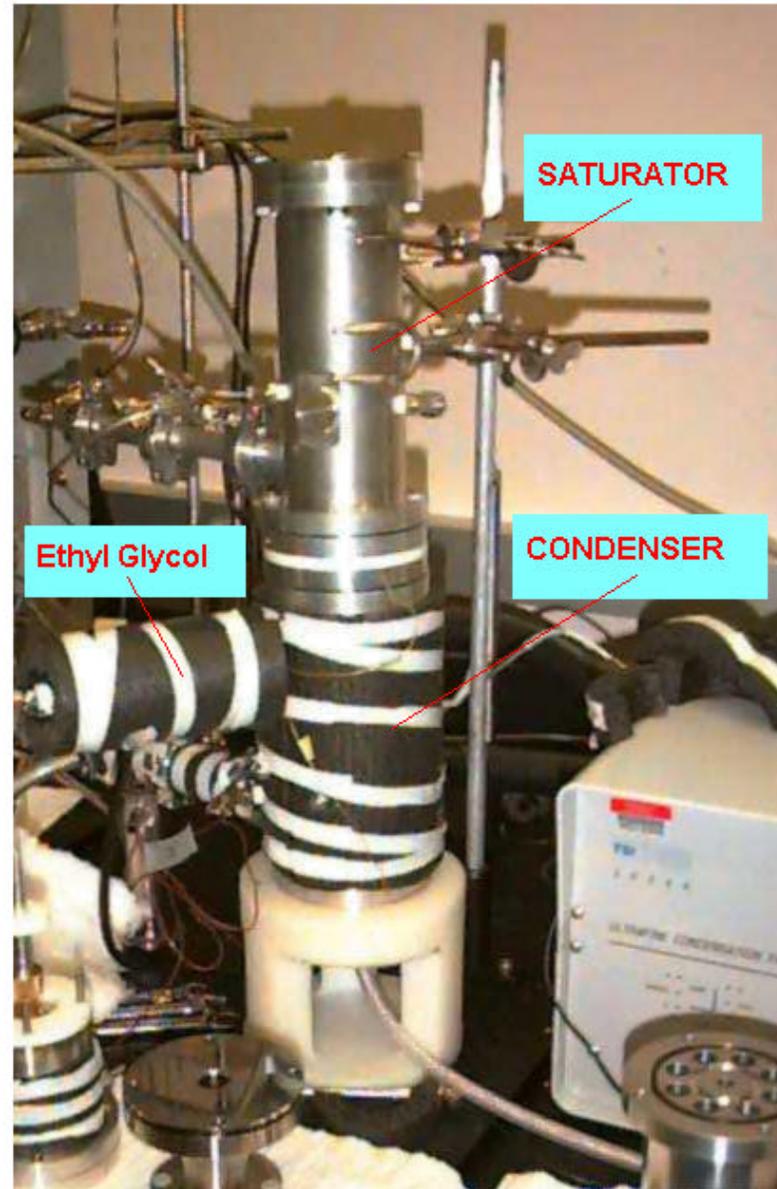


Figure 6

A Molecular Approach to Vapor-to-Liquid Nucleation: Simulations of Evaporation and Condensation of Molecular Clusters

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Objectives

Long term goals

- Develop a theoretical framework for accurately predicting nucleation rates in multicomponent systems
- Determine what molecular processes control the rate of nucleation

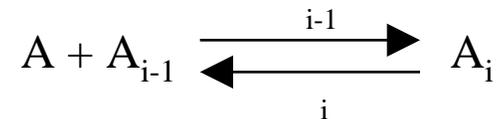
Short term goal

- Develop a molecular approach for calculating evaporation and condensation rates for molecular clusters

Classical Nucleation Theory

(Abraham, *Homogeneous Nucleation Theory*, 1974;
Seinfeld, *Atmospheric Chemistry and the Physics of Air Pollution*, 1986)

- Nucleation is treated as the evolution of cluster populations



- Condensation rate constant, k_{i-1} , is approximated by the gas kinetic collision rate of molecules with the cluster, assuming unit sticking probability

$$k_{i-1}^{\text{coll}} = (c/4) (4 r_i^2) n_1 = (c/4) (4 r_i^2) (p_1/kT)$$

c = average gas-phase velocity, r_i = cluster radius, n_1 = gas-phase monomer density

- Evaporation rate constant, k_i , is obtained from the condensation rate constant by detailed balance

$$k_i = k_{i-1} (N_{i-1}^{\text{EQ}} / N_i^{\text{EQ}})$$

Classical Nucleation Theory

(continued)

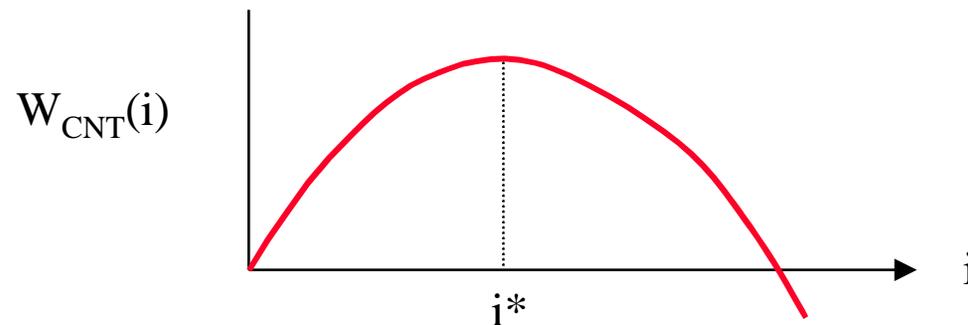
- Equilibrium cluster distributions approximated from bulk properties (e.g., solvation energies and surface tensions)

$$N_i^{\text{EQ}} = N_1 \exp(-W_{\text{CNT}}(i)/kT)$$

$$W_{\text{CNT}}(i) = -(4/3) r_i^3 (kT/v_1) \ln S + 4 \gamma r_i^2$$

v_1 = monomer volume in liquid, $S = N_1/N_1^{\text{EQ}}$ = supersaturation,
= surface tension, r_i = cluster radius

- Kinetics is assumed to be pseudo-steady state and nucleation rate is approximated by flux through critical cluster that has lowest equilibrium cluster population



Molecular Approach to Nucleation

(Lee, Barker, Abraham, *JCP* **58**, 3166, 1973;

Weakliem, Reiss, *JCP* **99**, 5374, 1993;

Hale, *Aust. J. Phys.* **49**, 425, 1996;

Kusaka, Wang, Seinfeld, *JCP* **108**, 3416, 1998)

- Nucleation is treated as the evolution of cluster populations (same as classical nucleation theory)
- Condensation rate constant, k_i , is approximated from the gas kinetic collision rate (same as classical nucleation theory)
- Evaporation rate constant, k_{-i} , is obtained from condensation rate constant by detailed balance (same as classical nucleation theory)
- Equilibrium cluster populations obtained by statistical mechanics (requires calculating cluster partition functions)
- Problem - “nucleation is a dynamical process and should be described by a dynamical theory rather than an equilibrium one” (Reiss, Tabazadeh, Talbot). In the equilibrium molecular approach, this problem requires that the cluster be operationally defined.

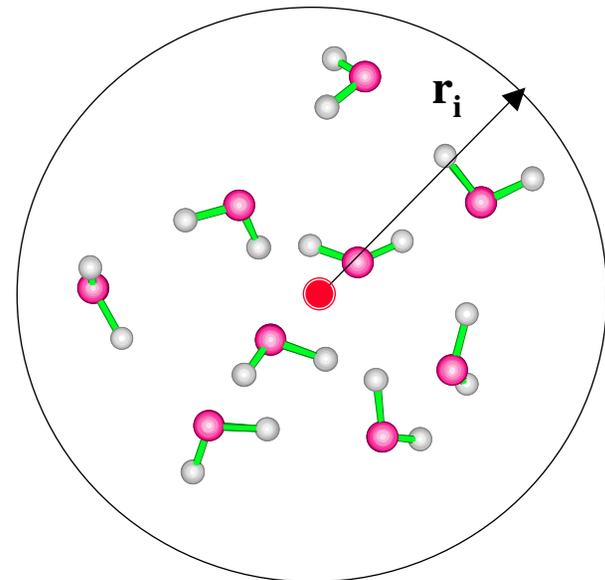
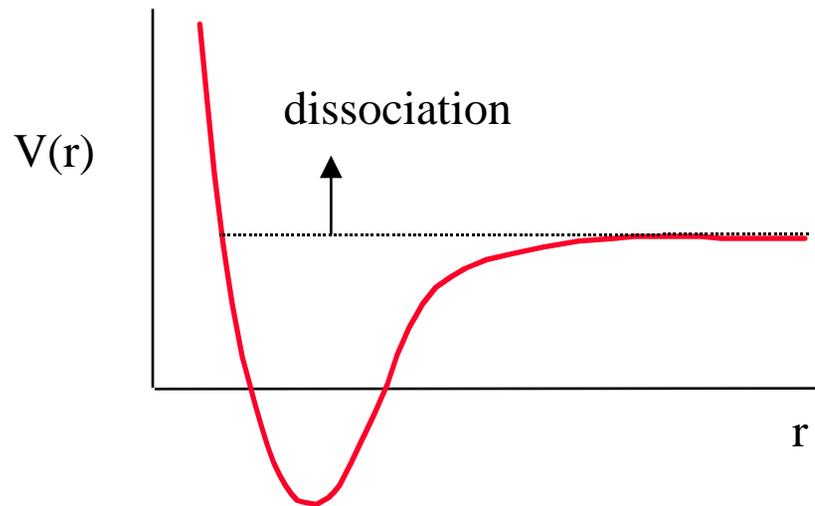
Physically Consistent Cluster

(Reiss, Katz, Cohen, *JCP* **48**, 5553, 1968;
Lee, Barker, Abraham, *JCP* **58**, 3166, 1973;
Reiss, Tabazadeh, Talbot, *JCP* **92**, 1266, 1990)

- The partition function of a dissociative cluster is arbitrarily large depending on the volume of the configuration space (entropy wins out).

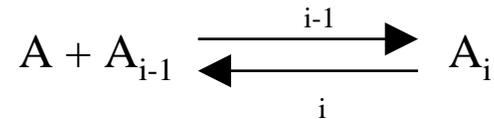
$$q(T) \propto \int dr \exp(-V(r)/kT)$$

- Cluster defined to lie within a spherical shell of radius r_i with center fixed on the center of mass of the cluster (Lee, Barker, Abraham).



Dynamical Nucleation Theory: A New Molecular Approach to the Kinetics of Nucleation

- Nucleation is treated as the evolution of cluster populations (same as classical nucleation theory)
- Dynamics of evaporation treated explicitly by approximating rate constant, k_{-i} , using variational transition state theory (VTST) - cluster radius, r_i , (or volume v_i) consistently defined by TST dividing surface that minimizes the reactive flux
- Condensation rate constant, k_i , consistently obtained using VTST (VTST obeys detailed balance) - requires equilibrium constants
- Nucleation rates obtained by solving kinetic equations



Variational Transition State Theory for Cluster Evaporation

- Cluster evaporation is treated as a gas-phase dissociation process



- Assume classical mechanics is adequate for this barrierless reaction
- Reactive flux approximated by the one-way flux through dividing surface separating reactants and products (TST). Dividing surface $S_i(r_{\text{cut}}, \mathbf{r}^{(i)})=0$ chosen as sphere of radius r_{cut} centered as center of mass of i-cluster

$$[\mathbf{r}^{(i)} = \{\mathbf{r}_j\}_{j=1, \dots, i}]$$

$$(S_i) = \sum_j (r_{\text{cut}} - |\mathbf{r}_j - \mathbf{R}_{\text{CM}}|)$$

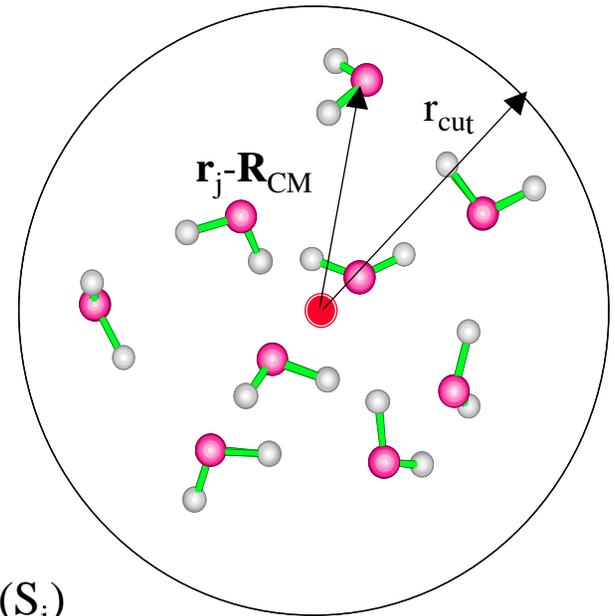
- Reactant partition function $q_i^R(r_{\text{cut}})$ and Helmholtz free energy $A_i(r_{\text{cut}})$ defined by:

$$q_i^R(r_{\text{cut}}) = \exp[-A_i(r_{\text{cut}})] = (i! h^{3i})^{-1} \int d\mathbf{r}^{(i)} d\mathbf{p}^{(i)} e^{-H} \delta(S_i)$$

- Evaporation rate constant defined by:

$$k_i(r_{\text{cut}}) = [i! h^{3i} q_i^R(r_{\text{cut}})]^{-1} \int d\mathbf{r}^{(i)} d\mathbf{p}^{(i)} e^{-H} \delta(S_i) \theta(\dot{S}_i) / 2$$

$$\delta(S_i) \theta(\dot{S}_i) = \int d\mathbf{p}^{(i)} \delta(\mathbf{p}^{(i)}/m) \cdot \delta(S_i) \theta(\dot{\mathbf{r}}^{(i)})$$



VTST for Cluster Evaporation (con't.)

- For the choice of spherical dividing surface, the evaporation rate takes the suggestive form:

$$j_i = (c/4) (4 \pi r_i^2) (-dA_i/dv_i)/kT = (c/4) (4 \pi r_i^2) (p_{int}/kT)$$

$$j_i^{coll} = (c/4) (4 \pi r_i^2) \rho_1 = (c/4) (4 \pi r_i^2) (p_1/kT)$$

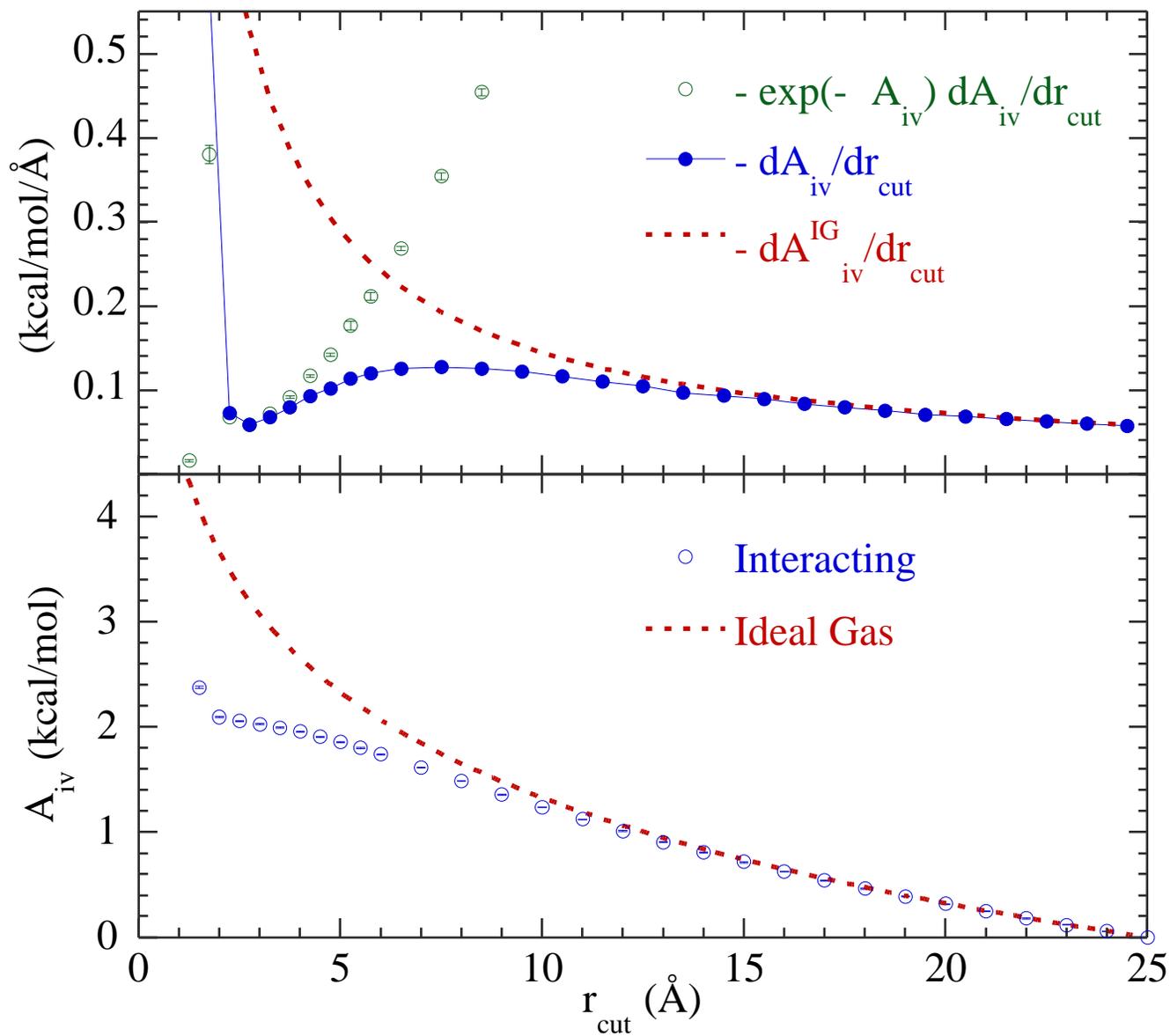
c = average gas-phase velocity, r_i = cluster radius,

ρ_1 = gas-phase monomer density, $v_i = 4 \pi r_i^3/3$

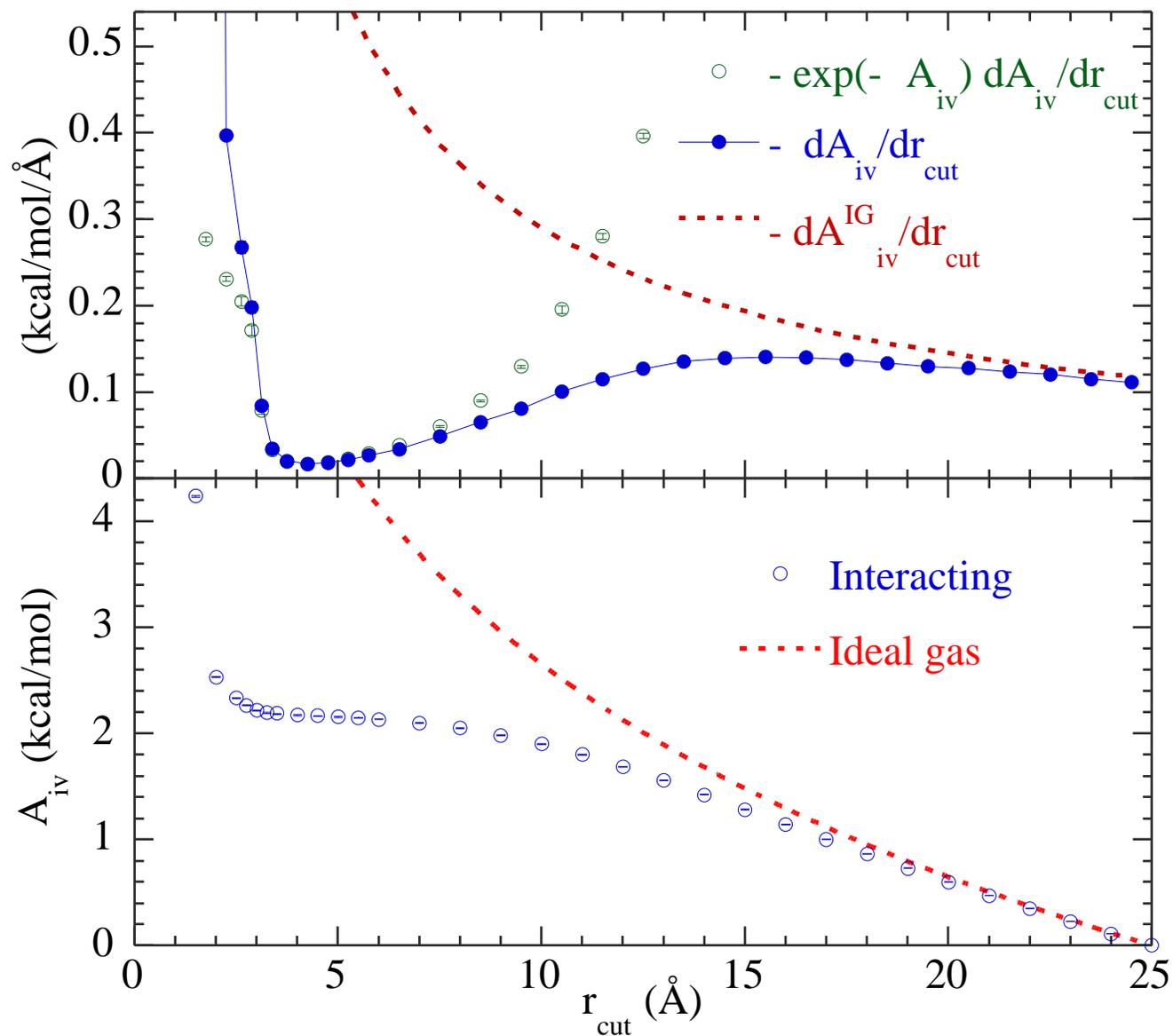
- Fundamental assumption of TST (Wigner, Trans. Faraday Soc. **34**, 29, 1938) guarantees that the TST approximation to the classical reactive flux is greater than or equal to the exact classical flux - best estimate of reactive flux can be obtained by variationally optimizing the dividing surface to minimize the reactive flux (Wigner, J. Chem. Phys. **5**, 620, 1937):

$$d[\exp(-A_i/kT) \rho_1]/dr_i = 0$$

Helmholtz Free Energy for Forming $(\text{H}_2\text{O})_2$ at 243 K



Helmholtz Free Energy for Forming $(\text{H}_2\text{O})_3$ at 243 K



Equilibrium Theory of the Vapor

(Reiss, Katz, Cohen, *JCP* **48**, 5553, 1968;
Reiss, Tabazadeh, Talbot, *JCP* **92**, 1266, 1990)

- Condensation rate constant obtained from evaporation rate constant using detailed balance

$$K_{i,i-1}^{\text{EQ}} = \frac{k_{i-1}}{k_i} = \frac{N_i^{\text{EQ}}}{N_{i-1}^{\text{EQ}}}$$

- Construct partition function for the entire (supersaturated) vapor system as a product of partition functions for bath molecules, monomers of condensing molecules, and clusters of varying sizes
- Equilibrium distribution is the most probable distribution subject to constraints (total number of molecules and volume of system are constant)

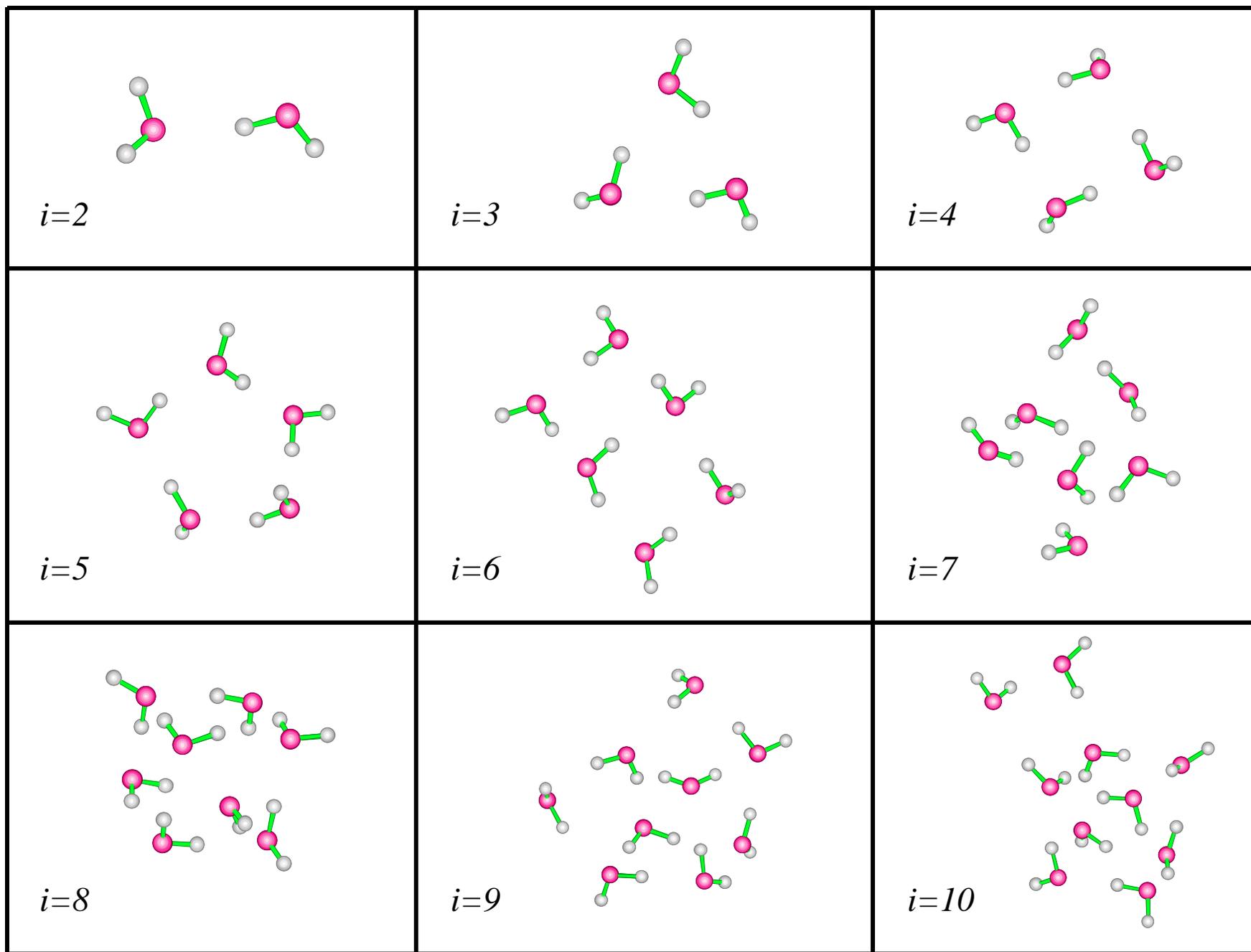
$$N_i^{\text{EQ}} = \exp[-W_{\text{REV}}(i)/kT]$$

$$= \exp\{-[A_i^\ddagger + p v_i^\ddagger - kT \ln(i^{3/2} V) - i\mu_1]/kT\}$$

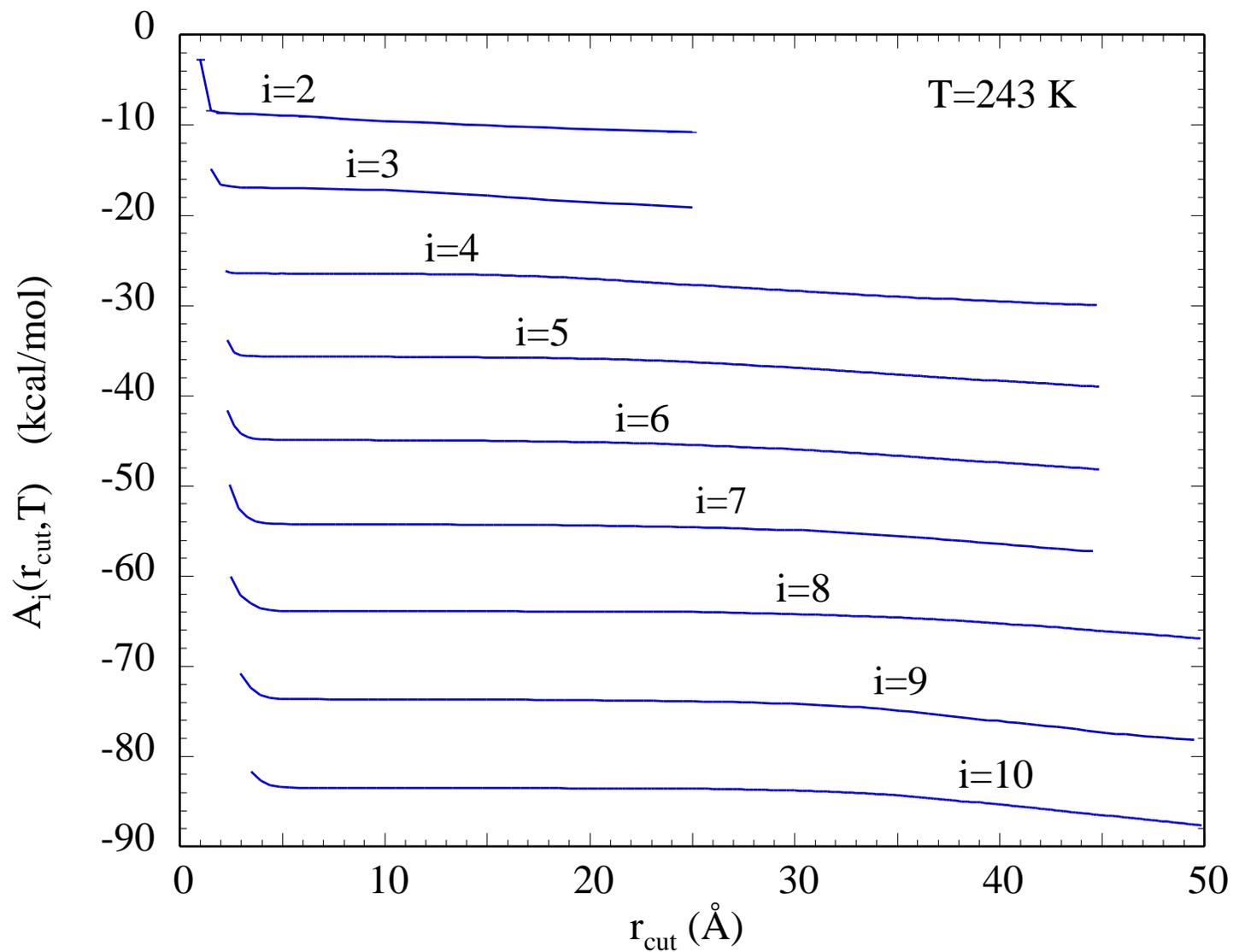
$$N_1/V = q_1 \exp(\mu_1/kT)$$

p = system pressure, μ_1 monomer chemical potential,
= monomer trans. p.f., q_1 = monomer p.f. (trans. & rot.)

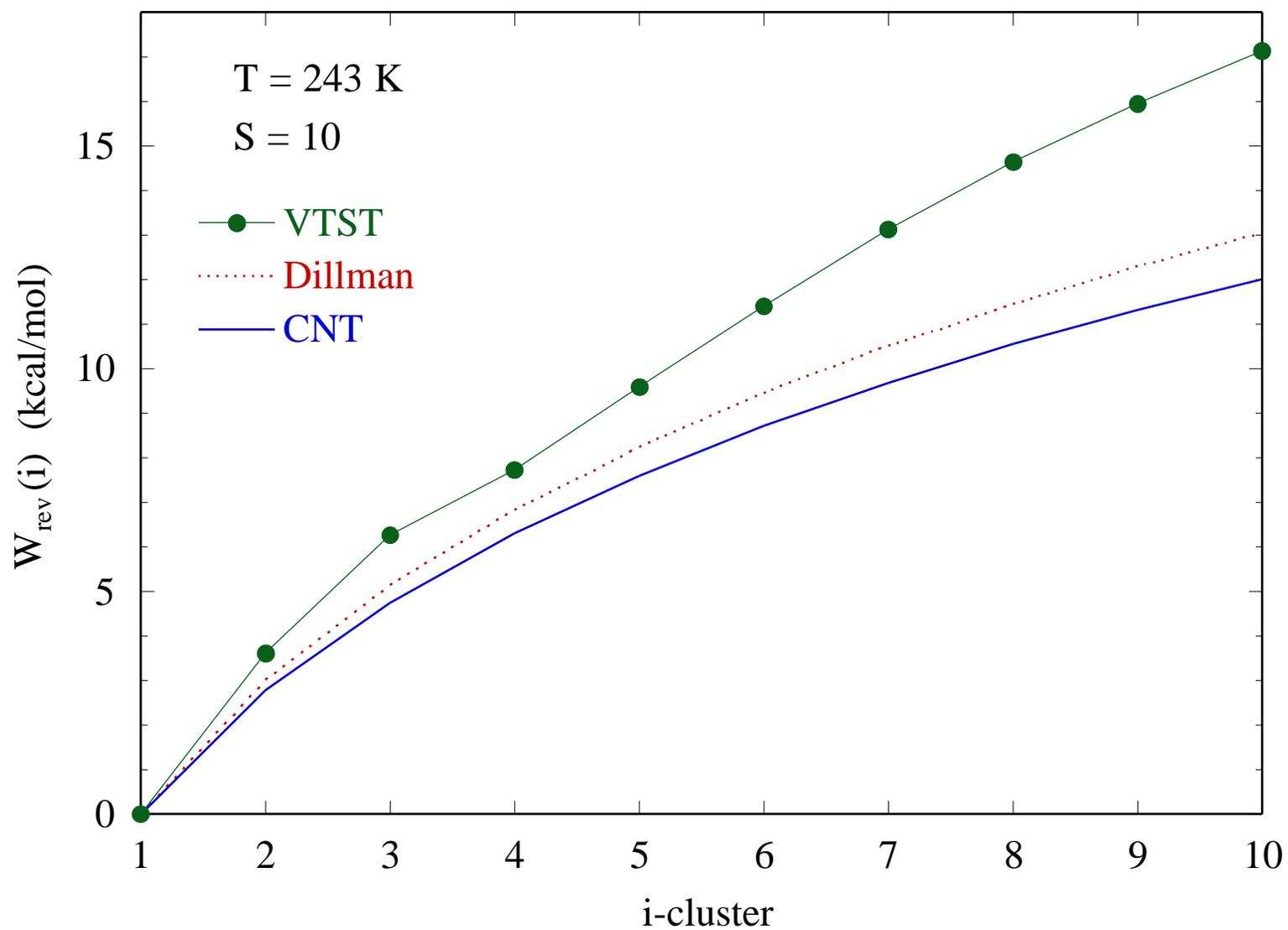
Probable Configurations at T = 243 K



Helmholtz Free Energy for Forming $(\text{H}_2\text{O})_i$ ($i = 2 - 10$) at 243 K



Reversible Work for Forming $(\text{H}_2\text{O})_i$ ($i = 2 - 10$)



Kinetics of Water Cluster Evaporation and Condensation

(T = 243 K, S=10)

i	r_i (Å)	$(-dA_{iv}/dv)$ (torr)	i (10^9 s^{-1})	i (10^7 s^{-1})	$K_{i-1,i}^{\text{EQ}}$	i/i^{coll}
2	2.8	32000	160	6.9	0.0004	0.89
3	4.3	4000	49	17	0.0034	0.90
4	5.8	210	4.7	18	0.039	0.54
5	5.8	450	10.0	22	0.023	0.66
6	6.3	490	12.8	26	0.021	0.66
7	6.8	310	9.4	29	0.031	0.62
8	7.5	190	7.2	26	0.037	0.46
9	8.0	120	5.2	33	0.064	0.51
10	8.5	96	4.6	28	0.061	0.38

Summary and Future Directions

- New molecular theory of nucleation kinetics has been developed - cluster is defined by spherical shell that minimizes flux
- New theory shows the rate of evaporation is proportional to the rate of change of the free energy with respect to shell radius (Previous molecular theories assumed free energy was insensitive to radius of shell enclosing cluster)
- Computationally tractable approach for water cluster evaporation (and condensation)

- Nucleation rates for water nucleation will be compared with new experimental data (Mikheev, Laulainen, Barlow)
- Extend methods to binary nucleation (ammonia - water and sulfuric acid - water) and to ternary nucleation (sulfuric acid - water - ammonia)

Accurate ab initio Electronic Structure Calculations of the Interactions of Water, Ammonia, and Sulfuric Acid Molecules

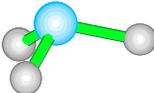
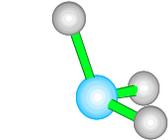
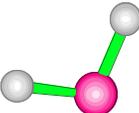
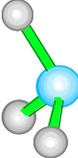
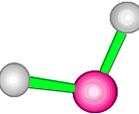
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Objectives

- Develop an understanding of the level of theory needed to accurately predict energies for interaction water, ammonia and sulfuric acid molecules
- Obtain accurate interaction energies for use in developing analytic potential energy functions

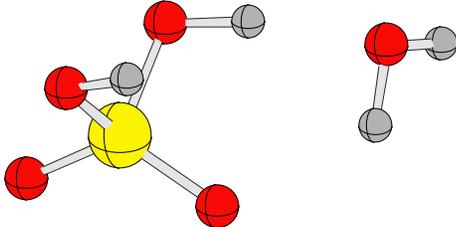
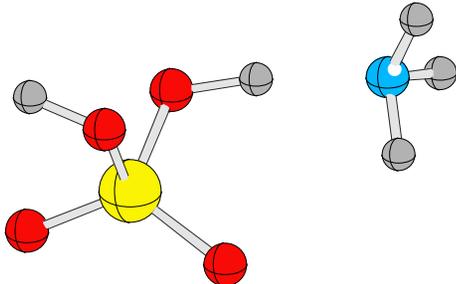
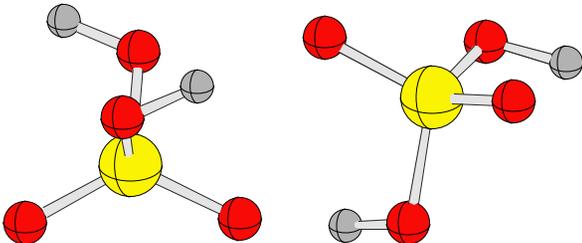
Equilibrium Geometries and Interaction Energies for Ammonia and Water dimers & mixed clusters

- Moller-Plesset second order perturbation theory (MP2) using correlation consistent basis sets (aug-cc-pVnZ, $n=D, T, Q, 5$)

	Binding Energy (kcal/mol)		
$\text{NH}_3\text{-NH}_3$	3.1		
$\text{H}_2\text{O-H}_2\text{O}$	4.9		
$\text{NH}_3\text{-H}_2\text{O}$	6.5		

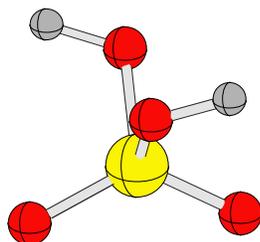
Equilibrium Geometries and Interaction Energies for Sulfuric Acid interactions with Water, Ammonia, and Sulfuric Acid Molecules

- Moller-Plesset second order perturbation theory using correlation consistent basis sets (aug-cc-pVDZ+d) with addition d functions used for sulfur atoms

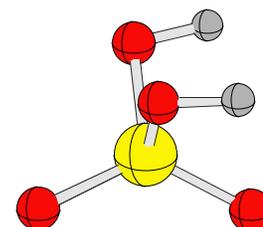
	Binding Energy (kcal/mol)	
$\text{H}_2\text{SO}_4\text{-H}_2\text{O}$	12.8	
$\text{H}_2\text{SO}_4\text{-NH}_3$	17.0	
$\text{H}_2\text{SO}_4\text{-H}_2\text{SO}_4$	17.7	

Effect of SOH Dihedral Angles on Relative Energies* (kcal/mol)

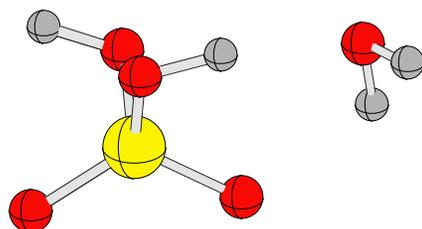
(MP2/aug-cc-pVDZ+d)



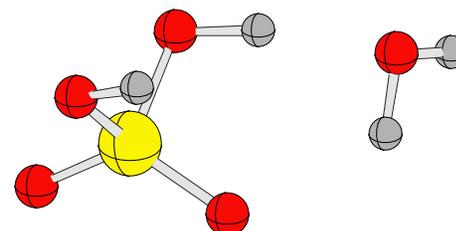
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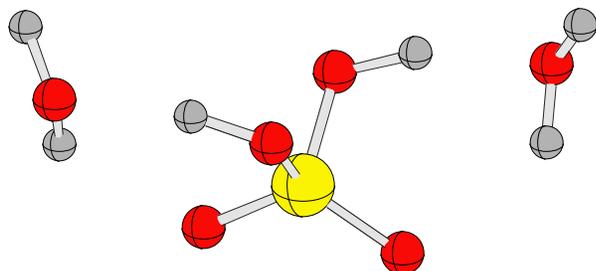
1.3



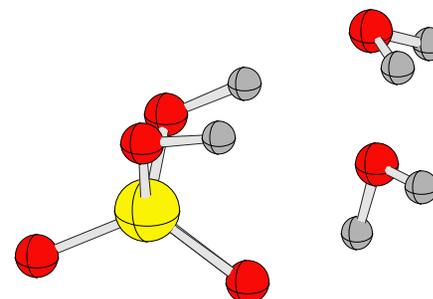
-12.7



-11.5



-25.1



-25.1

* All energies are relative to the sulfuric acid in its minimum energy geometry (upper left figure) and water molecules in their equilibrium geometry infinitely separated from sulfuric acid and each other.

Dependence of Potential Energy on SOH Dihedral Angles

